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Epitaxial Growth of a Highly Conductive Charge Transfer Complex from Vapor Phase —TTF-TCNQ—

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The epitaxial film of 1 : 1 radical cation-radical anion salt of TTF and TCNQ was prepared on KCl single crystal by vacuum deposition and the structure of the film as well as the nucleation mechanism have been investigated by means of electron microscopy and diffraction.

The b- or a-axis of the crystal is parallel to the [110] direction of KCl. Some anomalous diffuse scatterings were observed along the normal of the most conductive b-axis direction and the causes have been discussed.

KEY WORDS: Organic metal/ Diffuse scattering/ Reciprocal wall/
Nucleation/ Epitaxial film/

INTRODUCTION

The epitaxial growth of sublimable organic semiconductors has been investigated by the present authors.^{1,2)} They advocated that the organic molecule adsorbed on a crystalline substrate can decide the orientation of the epitaxial film. The molecular registry to the array of atoms or ions on the substrate surface correlates to the axial direction of overgrown crystals. When the multiple preferred orientations of molecules are allowed, the epitaxial growth in plural orientations takes place according to the registry of the adsorbed molecules. Chaudhari *et al.*³⁾ have reported that a charge transfer complex of 7,7,8,8-tetracyanoquinodimethane (TCNQ) with 2,2-bis-1,3-dithiole (TTF) (Fig. 1) sublimates in poor vacuum without decomposition and forms an epitaxial film on NaCl. The purpose of this work is to ascertain that the principle given for the epitaxial growth of organic crystals can be applied to the case of charge transfer complex composed of two different kinds of molecules. At the same time, the structure of the epitaxial film of low dimensional organic metals will also be investigated. The crystal structure analysis of TTF-TCNQ single crystal has been performed by Kistenmacher.⁴⁾ The crystal has unit cell constants; $a=12.298$ Å, $b=3.819$ Å, $c=18.468$ Å, $\beta=104.46^\circ$ and belongs to space group of $P2_1/c$.

EXPERIMENTAL

A stoichiometric mixture of commercially supplied TCNQ and TTF in chemical grade was solved in acetonitrile and kept at room temperature for a week. After the sol-

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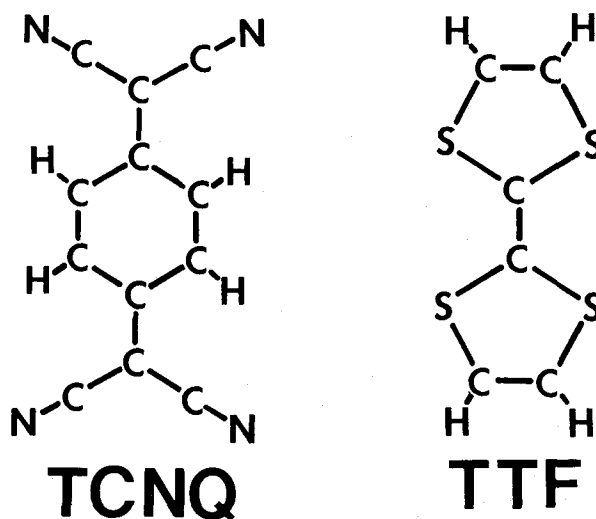


Fig. 1. Structure of TTF and TCNQ molecules.

vent was slowly evaporated some black needle crystals were obtained and the crystals were identified to be 1 : 1 complex of TTF-TCNQ by X-ray powder diffraction. A part of the powder was placed in a quartz crucible and evaporated in a vacuum of 1×10^{-4} Pa. Some newly cleaved single crystals of sylvine (KCl) were fixed on a heating plate in the vacuum chamber and heated at 500°C for two hours in order to eliminate surface contaminants. The temperature of KCl was reduced to a room temperature and the TTF-TCNQ was gradually evaporated by heating the crucible with wired tantalum and deposited on the KCl substrates. During the whole process vacuum was kept at the same order. The thickness of the deposited film was monitored by a quartz microcrystal balance located near the heating plate. The films were stripped off on pure water by dissolving the substrate KCl and fixed on copper grids directly or on some goldcoated micrigrids for the observation by electron microscopy or for electron diffraction. The gold film covering the frame of the grids was also used for a precise determination of the lattice distances as a standard for calibration of camera constant for electron diffraction. The electron microscopes used were JEM-100C or JEM-200CX equipped with a minimum dose system for the reduction of radiation damage of specimens during the observation.⁵⁾

RESULTS

The vacuum deposited films obtained by sublimation of TTF-TCNQ powder are composed of many microcrystals oriented in two directions crossing at right angles with each other as shown in Fig. 2. A high resolution electron diffraction pattern (HRED) of this film whose thickness is about 600 Å is also reproduced in Fig. 2(b). The HRED exhibits a square lattice with a periodicity of 3.78 Å^{-1} and on the two main axes diffraction spots make arrays with an intervals of 12.29 Å^{-1} . To the HRED contribute many crystals but the selected area electron diffraction (SAED) conveys the structure information from a small region of the specimen. The SAED showed a fiber pattern as shown in Fig. 3.

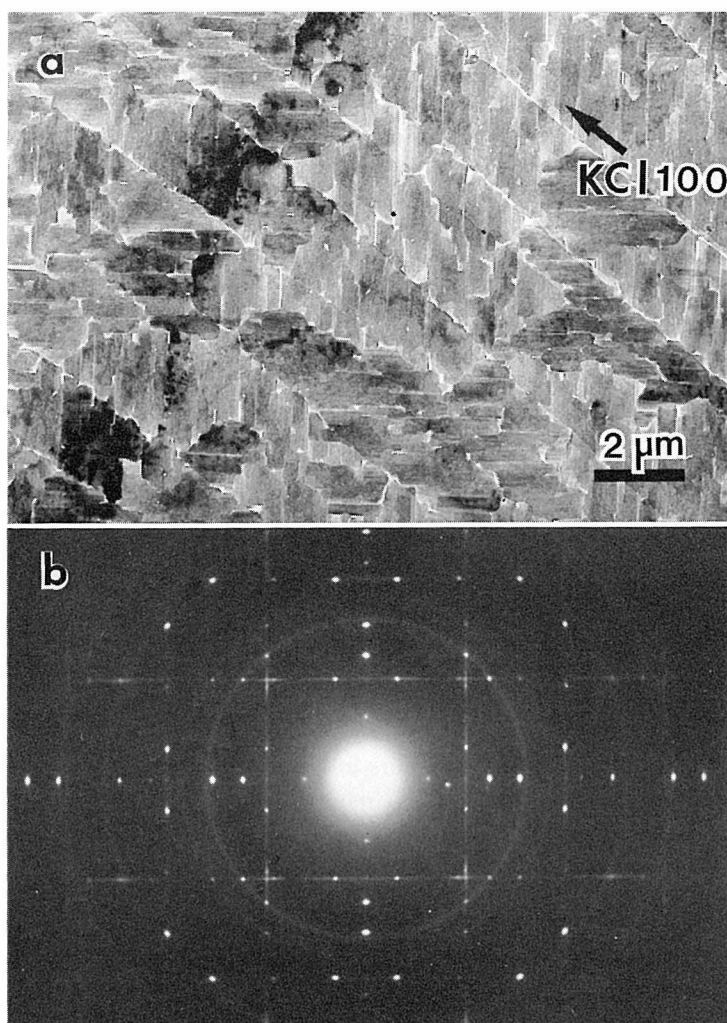


Fig. 2. (a) Electron micrograph of the epitaxial film of TTF-TCNQ. Film thickness is 600Å.
(b) High resolution electron diffraction from the crystals in (a).

It is clear that the reciprocal lattice units revealed by the SAED are 12.29 \AA^{-1} and 3.78 \AA^{-1} and that the HRED in Fig. 2(b) is composed of two sets of similar patterns superimposed on each other. As the crystal was tilted with a aid of a goniometer stage around the b^* -axis in the HRED, the feature changed gradually. At the region of the tilting angle of 12–15 degrees the intensities distribution of the spots array on the equator which is perpendicular to the tilting axis indicated that another main axis in the reciprocal lattice came to fit the Ewald sphere and fulfilled the diffraction conditions. The HRED with a tilting angle of 14° are shown in Fig. 4. The periodicity of the spots array is 11.9 \AA^{-1} and therefore the equator assumes to represent the a^* -axis of TTF-TCNQ crystal at this angle. These situation is illustrated in Fig. 5. The fiber period 3.78 \AA^{-1} is tentatively taken as the b^* -axis which is parallel to one of the $[110]$ axis of the substrate

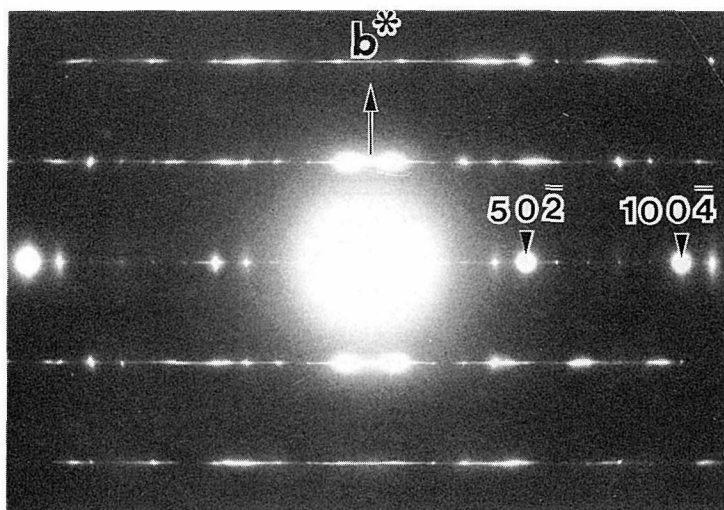


Fig. 3. Selected area diffraction pattern from the area of single orientation of TTF-TCNQ.

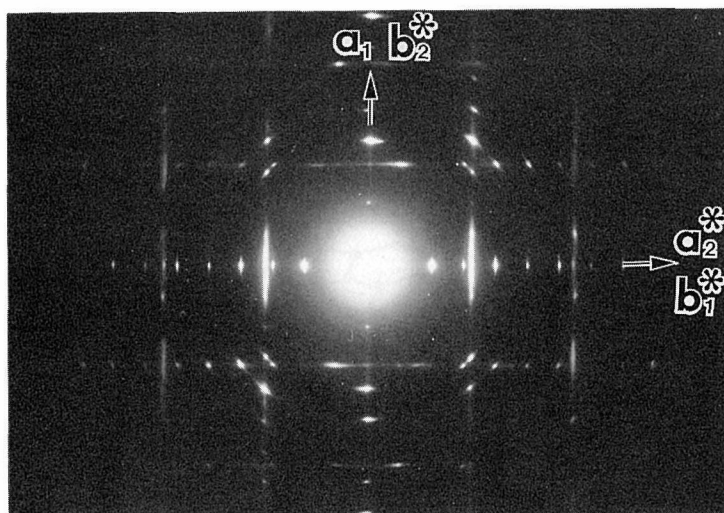


Fig. 4. High resolution electron diffraction pattern from TTF-TCNQ tilted 14° around the vertical b^* -axis.

KCl. The mutual correlation of TTF-TCNQ and KCl is schematically represented in Figs. 6 & 7.

DISCUSSION

The SAED pattern (Fig. 3) has shown that the reciprocal lattice assumes to have the unit cell of 12.29 \AA^{-1} along the equator and 3.78 \AA^{-1} along the meridian. The reciprocal unit dimension derived from the X-ray data are 11.909 \AA^{-1} and 3.819 \AA^{-1} for a^* and b^* respectively. However, the unit cell constant of the a -axis is 12.298 \AA and this value

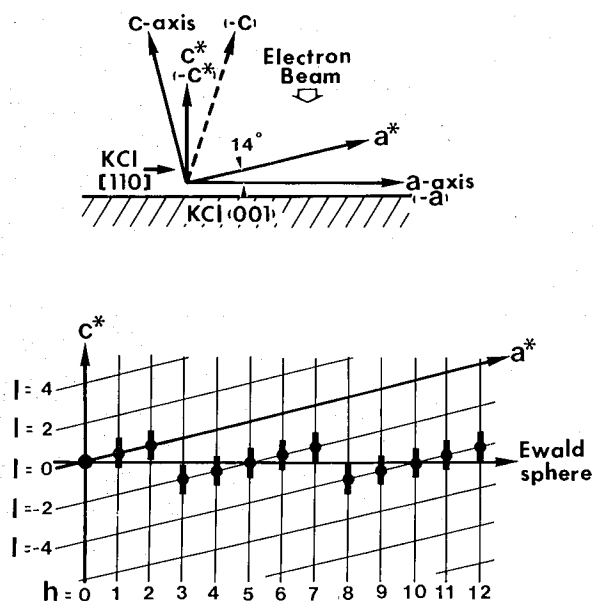


Fig. 5. (a) Relationships between the real and the reciprocal lattices of TTF-TCNQ epitaxial film on KCl. The direction of a -axis coincides with $[110]$ of KCl. (b) The reciprocal lattice points of TTF-TCNQ intersecting the Ewald sphere can be observed in the electron diffractions shown in Figs. 2 & 3.

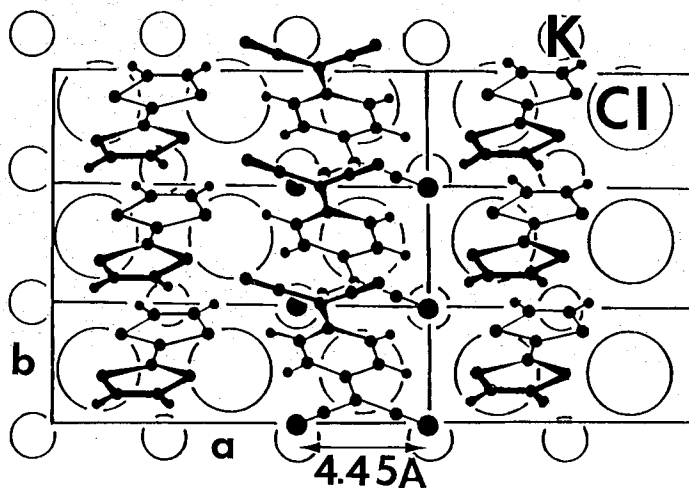


Fig. 6. Mutual orientation of both crystal lattices of substrate KCl and TTF-TCNQ. TCNQ in the center keeps its two nitrogens just on the potassium ions.

coincides well with the inverse of the periodicity of the spots array on the equator of the HRED pattern in Fig. 2. Accordingly it is supposed that the a -axis of TTF-TCNQ crystal, which belongs to a monoclinic system, lies in parallel with the substrate plane and that the diffraction spots appeared in Fig. 2 are caused by the intersection of the Ewald sphere and the elongated reciprocal lattice points. This situation is illustrated in Fig. 5.

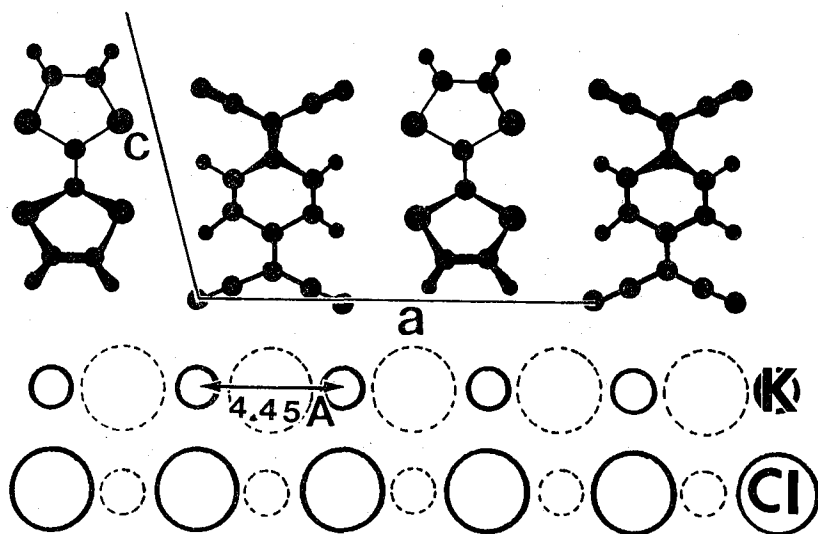


Fig. 7. Edge-on view of the orientations of TTF-TCNQ on KCl. TCNQ and TTF lean forward and backward from the plane of the figure respectively.

The elongation of the interference region around each reciprocal lattice point is due to the smallness of the dimension along the depth direction of the film. The a^* -axis is tilted by 14° with respect to the a -axis which is parallel to the substrate plane. When the film is tilted around the b^* - or b -axis, the a^* -axis comes to fit the Ewald sphere and the diffraction spots of $\{h00\}$ will appear, as actually observed in the HRED pattern given in Fig. 4.

The fiber period obtained from the HRED is 3.78 Å whereas the unit cell constant along the b -axis has been reported to be 3.819 Å. As mentioned above, two simple patterns are superimposed on each other with an angle of 90° in HRED shown in Fig. 2. Accordingly, when the film is tilted around one of the b^* -axis, the change of the pattern due to the rotation of the crystal around the a -axis can also be observed at the same time. If a longer period than 3.78 Å exists in the perpendicular direction to the a -axis it should be observed in the course of tilting. Practically, however, the period of this kind has not been observed during the careful search by tilting the crystal in the angle range of $\pm 30^\circ$. Therefore, it was reasonably concluded that the fiber period of 3.78 Å appeared in the electron diffraction pattern corresponds to the period along the b -axis of the crystal in the epitaxial film. In conclusion the film makes its ab -plane parallel to the substrate surface and the unit cell dimension along the b -axis is slightly shorter than that of the single crystal reported by Kistenmacher *et al.*⁴⁾ The relationships between the substrate lattice and the epitaxial film can be derived from these facts and axial correlation. Figs. 6 & 7 show such mutual positions. Though two sets of patterns are superimposed in HRED, one set is illustrated in these figures and the other can be obtained by 90° rotation of the lattice of organic crystal with respect to that of the substrate and the situation is the same as the former because of the symmetry of the substrate crystal.

The principle of the epitaxial growth proposed by Uyeda *et al.*¹⁾ for organic crystals can also be applied here to explain the nucleation mechanism and the epitaxial directions of TTF-TCNQ crystal on KCl substrate though the crystal is composed of two different

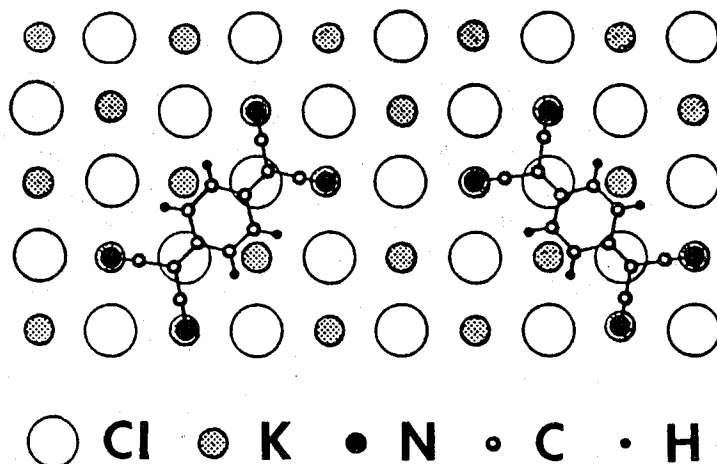


Fig. 8. The molecular orientations of TCNQ molecule on KCl at the most stable positions. (See ref. 1.).

kinds of molecules. In case of the epitaxial growth of TCNQ crystal on KCl, TCNQ molecule adsorbed flat at first making its molecular plane parallel to the substrate surface. At that time, four CN groups of the molecule interact with potassium ions on KCl crystal surface. Some charge transfer from the substrate to the molecule might occur and plays an important role in defining the molecular orientations. The most preferred adsorption state derived from the electron microscopical data is reproduced in Fig. 8. In this case plural number of axial correlations are permissible due to the symmetries of the molecule, substrate and TCNQ crystal. On the other hand some attempts to obtain an epitaxial film of TTF crystal by vacuum sublimation have turned out to be unsuccessful because the high volatility of the material disturbs the crystal formation on KCl kept at the room temperature. On the contrary, molecular plane of TCNQ in the epitaxial film of TTF-TCNQ is tilted about 35° with respect to the ab-plane and consequently to the substrate surface as shown in Figs. 6 & 7. In this situation only two CN groups of TCNQ can come in contact with the potassium ions and the other two are apart from the substrate. This can be interpreted to be due to the cooperation of TTF molecules. The molecular planes of TTF and TCNQ make an angle of about 80° in the crystal and they keep contact with each other by sides so that their side view becomes a cross. Therefore, TCNQ adsorbed flat at first on KCl must rise in order to keep contact with TTF which came after or together at the side of TCNQ molecules. TTF molecules come onto the substrate prior to the adsorption of TCNQ molecule are considered not to adsorb or to find no stable position on KCl because of their high volatility or weak interaction with the KCl. Only when the TCNQ molecule is located on the substrate, the TTF can be settled on the surface. The edge on view of the adsorbed state of both molecules on KCl is shown in Fig. 7. TCNQ has four nitrogens and the shorter N-N distance is 4.407 Å in TTF-TCNQ crystal. This distance fits well to the K-K separation of 4.449 Å on KCl along [110] direction. The a-axis is parallel to the line running through these two nitrogens. As the result, the a-axis of TTF-TCNQ becomes parallel to the [110] of KCl. The b-axis makes an angle

of 34° with respect to the normal of the TCNQ molecular plane. When TTF comes close to TCNQ side by side, TCNQ should get up keeping the contact of two nitrogens with the substrate potassium ions. The secondly coming TCNQ stacks in parallel with the first one and at this moment the direction of the b-axis, which coincides with the axis of molecular column, is defined. The interaction of TTF with substrate might be weaker than that between TTF and TCNQ as deduced from the results of the attempt to make the vacuum deposited film of TTF. However, the molecular center of TTF comes between two Cl ions of KCl and it seems to be a stable position for the molecule which behaves as a cation in the crystal. It can be given as a conclusion that the direction of TTF-TCNQ crystal axis epitaxially grown on KCl is defined by the oriented adsorption of TCNQ followed by the addition of TTF.

The shrinkage of the b-axis in the epitaxial film is considered to stem from a slight change of angle between the normal of molecular plane of TCNQ and the b-axis or by the change in molecular intervals in each molecular column in the crystal. It is considered that a small amount of charge redistribution on molecules caused by the interaction between molecules and the substrate produces such new molecular stacking.

The most prominent feature of the HRED is the existence of sharp streaks on the diffraction spots of the layer lines. Among many possibilities to produce the streaks on diffraction spots, stacking fault, which are introduced during the crystal growth, is most plausible as has been discussed by Kobayashi *et al.*⁶⁾ If the streaks are originated by the existence of some stacking faults, they can be identified by tilting the crystal against the incident electron beam because the streaks can be observed only under some special conditions and they usually disappeared when the faulted plane is not parallel to the incident beam direction. The streaks observed in the present specimens appeared even when the crystal was tilted around the b- or a-axis as clearly seen in Fig. 4. This fact indicates that the interference regions are not linear but make two dimensional walls by mutual fusion in the reciprocal space, which are produced by some linear object in the crystal as the scattering source. Two main causes can be considered for such scattering sources.

TTF-TCNQ crystal is one of the electronically low dimensional organic metals. Such low dimensional substances mostly have electron instabilities which tend to cause the phase transition of the crystal and they show anomalous diffuse scattering at some temperature ranges in their electron- or X-ray diffraction patterns. In order to determine whether the streaks are due to the electronic instability or not, the temperature dependence of the scattering pattern should be studied with a use of low temperature stage for electron microscopy.

The other and more plausible cause of the streaks is the structural defects other than the stacking fault. The X-ray structure analysis of TTF-TCNQ has revealed that TTF and TCNQ make their own molecular columns in the crystal and the columns are parallel to each other or the b-axis. One kind of the column interact with the other through a charge transfer force which does not occur at some special or unique points on the molecules but at column sides in different kind. Therefore, a slight glide of the columns with respect to a neighboring one along the column axis may easily takes place in the crystal and the shifted molecular columns can act as linear scattering sources causing

a reciprocal wall. The strong interaction between the substrate and TCNQ molecule causes such defects in crystal. One adsorbed TCNQ on KCl can act as a nucleus of the column growth and defines the axial direction. Another TCNQ adsorbed at other site on KCl near the first molecular column also behaves as a nucleus of other column. The molecular columns thus produced are parallel or perpendicular to each other according to the initial orientation of TCNQ. In the former case, they assume to form a crystal. However, the ordering of the columns, which have independently grown from each adsorbed molecule at different sites, is not always regular in the tranverse direction to the column axis due to the existence of misfit between the substrate lattice and the arrangement period of molecules in the column. This irregularity is the cause of the streaks observed in the electron diffractions.

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